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# Influence of Volatile Metal Carbonyls on the Reactions of Thermal Radicals in the $C_4H_{10}$ + Recoil T System*

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*The addition of $Ni(CO)_4$ and $Fe(CO)_5$ to the $C_4H_{10}$ + recoil T system causes remarkable increase of ethylene-T and light hydrocarbons-T yields. The effect of metal carbonyls on product yield variation has been ascribed to an intermediate containing the metal and the radicals produced in the reactions. By the use of inert moderators and pressure effect, which enhance the radical density, the essential role of T· and alkyl radicals as limiting reactants is discussed.*

## Introduction

It has been previously reported [1] that the product distribution from the reaction of recoil tritium atoms with hydrocarbons could be significantly modified by the presence of small amounts of $Ni(CO)_4$ in the reacting mixture. The same effect has been observed when $Fe(CO)_5$ is added to the reacting system. Due to the wide use of Ni and Fe, both as metal and metal derivatives [2] to catalyze a large number of reactions, the understanding of the behaviour of such systems could be of great interest both for practical and theoretical purposes.

In this paper are reported the results of some investigations on the system $T^* + C_4H_{10} + Me(CO)_n$ performed under a variety of experimental conditions in order to test the reaction mechanism previously suggested [1]. The butane + T* system has been chosen to test the mechanism because the reactions of butane with recoil T have been thoroughly studied and the behaviour of the system is well known [3].

## Experimental

High purity chemicals were used for the experiments Butane (Rivoira Co.), $Ni(CO)_4$ (Strem Chemical Inc.), $Fe(CO)_5$ (Fluka A.G.), $^3He$ (Monsanto) and Ne (Matheson) were used without further purification.

Standard vacuum techniques were used to prepare the samples for the experiments.

Using $Ni(CO)_4$ special care was necessary in outgassing the quartz vessels before filling, to avoid the formation of a metallic film on the walls. The quartz vessels containing the reaction mixture were bombarded with a thermal neutron flux of $0.8 \times 10^{11}$ n cm$^{-2}$ sec$^{-1}$ for three hours in the Triga Mark II Reactor of the University of Pavia. The bombardment was carried out in the reactor pool outside the reflector at a water temperature ⩽30 °C. The samples were analyzed by radio-gas-chromatography on a 4m Chromosorb 102 column. The temperature was kept at –30 °C until $CH_3T$ was eluted and then increased to 150 °C at a rate of 25 °C min$^{-1}$. Other details on the analysis are reported elsewhere [1, 4].

In some particular experiments a Ni mirror was laid out on the ampoule walls slowly heating the ampoule containing the desired amount of $Ni(CO)_4$. Some vessels containing $C_4H_9T + Ni(CO)_4$ or $C_4H_{10} + Ni(CO)_4 + HT$ were heated in a thermostatic bath at 60 °C or 80 °C for times ranging from 8 to 24 hours, to test the thermal stability of the system and the effect of the $Ni(CO)_4$ decomposition products.

## Results

In a previous paper [1] the product yields were reported as relative yields referred to the activity of the parent = 100. While such a way better evidentiates the yields variations, it does not show the actual yields, especially the variation of the activity of the parent molecule and the total activity. For this reason the product yields in the following Tables are reported as percentage of total volatile activity as detected in a butane + $^3He$ sample free from additives [5]. The activity of each sample was corrected for the neutron flux (monitored by a Co probe attached to each vessel), for recoil loss, for HT from walls and $^3He$ content where necessary [6].

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TABLE I. Results of the Reactions of T* + $C_4H_{10}$ with Various Additives.

| *Reactant and additives* (Pressure in KPa) | | | | | | |
|---|---|---|---|---|---|---|
| Butane + $^3He^a$ | 101.59 | 101.59 | 101.59 | 101.59 | 101.59 | 101.59 |
| $Ni(CO)_4$ | – | 9.33 | – | 26.64 | – | – |
| $Fe(CO)_5$ | – | – | 4.00 | – | – | – |
| Metal Ni (mirror) | – | – | – | – | yes | – |
| CO | – | – | – | – | – | 27.97 |
| *Tritiated Products* (as % of total volatile activity) | | | | | | |
| HT | 63.9 | 49.2 | 51.2 | 49.0 | $59.4^b$ | 63.2 |
| $CH_3T$ | 2.1 | 5.4 | 4.8 | 5.3 | 1.9 | 2.2 |
| $C_2H_3T$ | 1.0 | 4.5 | 3.9 | 4.6 | 1.1 | 1.2 |
| $C_2H_5T$ | 2.5 | 4.0 | 3.4 | 4.2 | 2.6 | 2.6 |
| $C_3H_7T$ | 2.4 | 4.0 | 3.7 | 4.0 | 2.4 | 2.5 |
| $C_4H_9T$ | 25.7 | 29.5 | 28.1 | 28.3 | 24.6 | 24.8 |
| $C_5$–$C_6$ | 2.1 | 0.3 | 0.8 | 0.6 | 2.8 | 2.9 |

[a] The partial pressure of $^3He$ was 2.66 KPa. [b] Small percentage of HT adsorbed on the walls, as explained in the text.

TABLE II. Oxygen Effect on T* + $C_4H_{10}$ System with and without a Metal Carbonyl.

| System | | Products | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $^3He$ + Butane$^a$ Additives | P(KPa) | HT | $CH_3T$ | $C_2H_3T$ | $C_2H_5T$ | $C_3H_7T$ | $C_4H_9T$ | $>C_4$ |
| $O_2$ | 2.66 | 40.8 | 1.2 | 1.4 | 1.3 | 1.2 | 24.2 | tr |
| $O_2$<br>$Ni(CO)_4$ | 2.66<br>9.33 | 41.2 | 3.1 | 1.5 | 2.9 | 2.4 | 25.9 | – |

[a] Partial pressures: $^3He$ 2.66 KPa, Butane 101.59 KPa.

The first two columns of Table I show that when $Ni(CO)_4$ is a component of the reacting mixture, the HT yield decreases sharply together with the yields of hydrocarbons higher than $C_4$, while the yields of fragmentation products, particularly $C_2H_3T$ and the yield of the parent increase. Column three shows that the same effect is obtained when another volatile carbonyl, $Fe(CO)_5$, is present. The amount of carbonyl does not influence the extent of the reaction, as reported on column four. The last two columns show that the original product distribution is not affected either by a mirror of elemental Ni or by the presence of carbon monoxide.

The chromatographic analysis was not routinely extended to any compound with a retention time higher that $C_6$. In some instances the analysis was extended to higher retention time products which have found to be negligible. The percentages reported do not account for such products and the total activity fluctuations could not be ascribed to them.

When oxygen is added as radical scavenger to the $C_4H_{10}$ + T* system, the yields are supposed to be reduced to pure hot yields. On Table II is reported the effect of the added oxygen on both $C_4H_{10}$ + T* and $C_4H_{10}$ + $Ni(CO)_4$ + T*. The effects on both systems are comparable in spite of an apparent lower efficiency of the scavenger on the system containing $Ni(CO)_4$.

Many radical species are supposed to be involved in the thermal rearrangement of the fragments produced in concomitance of the reaction. Both inert moderators and the total pressure of the reacting system are likely to modify the spectrum of the thermal species. The inert moderators will reduce and, in case, eliminate the hot reactions by reducing the number of collisions of the hot atoms with the reactant, and hence will increase the number of thermal tritium atoms. Molecules and radicals labelled by hot atoms may have sufficient energy to undergo decomposition to smaller molecules or radicals. These excited species may be deactivated

TABLE III. Moderator and Pressure Effect on T* + $C_4H_{10}$ with and without $Ni(CO)_4$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *Reactant and additives* (Pressure in KPa) | | | | | | |
| Butane + $^3He^a$ | 26.92 | 26.92 | 200.00 | 200.00 | 13.33 | 13.33 |
| Ne | 320.00 | 320.00 | – | – | – | – |
| $Ni(CO)_4$ | – | 6.66 | – | 16.15 | – | 1.6 |
| *Tritiated Products* (yields in % of total volatile activity) | | | | | | |
| HT | 67.1 | 51.2 | 62.9 | 50.1 | 66.2 | 54.0 |
| $CH_3T$ | 1.9 | 5.2 | 2.1 | 6.0 | 2.7 | 5.2 |
| $C_2H_3T$ | 1.0 | 6.5 | 0.8 | 4.5 | 0.8 | 5.7 |
| $C_2H_5T$ | 2.9 | 4.8 | 3.0 | 4.2 | 3.5 | 4.8 |
| $C_3H_7T$ | 3.9 | 5.2 | 2.2 | 3.1 | 3.4 | 3.6 |
| $C_4H_9T$ | 19.3 | 24.4 | 26.2 | 32.1 | 23.2 | 27.1 |
| $C_5$–$C_6$ | 3.6 | 1.4 | 2.9 | tr.[b] | 3.8 | 0.7 |

[a] The $^3He$ pressure was in each sample reported to 2.66 KPa. [b] Yields reported as tr. were $\leq 0.2\%$.

by collision with the surrounding molecules. The total pressure of the system may then be used to increase or to decrease the yield of radical species from decomposition reactions. The results of moderator and pressure effects on the yield of various labelled species are reported in Table III. The influence of both moderators and pressure are particularly evident on methane and ethylene as shown in columns two, four and six.

## Discussion

The main effect of the added metal carbonyls ($Ni(CO)_4$ or $Fe(CO)_5$) to the butane + recoil T system are: the increase of the yield of labelled fragmentation products (mainly ethylene), the increase of the activity of the parent and the decrease of the yield of HT and higher hydrocarbons.

### *Influence of metal carbonyl decomposition products*

The metal carbonyls may be decomposed by the radiation field associated with the neutron flux, by the neutron themselves and by the recoil particles, via partially carbonylated intermediates. Metal particles are known to catalyze a large spectrum of reactions on hydrocarbon systems. Fragmentation of pentane upon hydrogenation of pentane–metal Ni complexes has been observed by Klabunde and coworkers [7]. Metal Ni and Fe catalyze the hydrogenolysis [8] and the hydrogenation [9] of saturated and unsaturated hydrocarbons, respectively, but such reactions generally require high temperatures [10, 11].

Some experiments have been performed in reaction vessels containing preformed Ni mirror on the walls to test the effect of metal particles. The results of such experiments, reported on the fifth column of Table I, show that the possible catalytic effect of the metal (on the ampoule walls) is not responsible for the observed change in the product distribution. The only observable effect of the Ni surface was the adsorption of about 3% of HT, which has been recovered by thermal desorption after all the volatile products were pumped off. Furthermore also the Ni particles produced by heating in thermostatic bath samples containing $Ni(CO)_4$ plus labelled butane or $Ni(CO)_4$ + HT + butane proved unable to form fragments or T-exchange products.

From the above results it can be stated that the change in the spectrum of the products of the reaction between recoil tritium and butane cannot be attributed to heterogeneous reactions of Ni or Fe particles, despite their wide catalytic activities.

The partially carbonylated species from the decomposition of the metal carbonyl have also been considered as possible cause of the observed shift of the product yields. If the above species are of primary importance for the observed change in the product spectrum, an increase of the amount of $Ni(CO)_4$ in the reacting system will increase the amount of reactive species and cause a further build-up of ethylene, fragmentation products and labelled parent, with an accompanying further reduction of HT. The data reported on columns two and four of Table I indicate that on increasing the concentration of the metal carbonyl from 8% to >20%, the yields of ethylene and fragmentation products do not increase. This finding, together with the observed lack of labelled products from the thermal decomposition of $Ni(CO)_4$ in butane-T or in a mixture of HT and butane, leads to the conclusion that the species from the decomposition of the carbonyl do not influence, on their own, the product distribution.

### *Metal Carbonyls as Vehicles of Thermal Radicals*

The recoil T atoms reacting with butane produce a wide spectrum of radicals, stable and excited molecules [12]. Unfortunately gas-phase reactions involving radical species and metal carbonyls are not known, whereas reactions of ionic species with pure and substituted metal carbonyls have been observed in gas phase for $Fe(CO)_5$ [13], for derivatives of both $Cr(CO)_6$ and $Mo(CO)_6$ [14] and for $Co(CO)_3NO$ [15]. A reaction between $Ni(CO)_4$ and fragments from butane has been recently observed in the ion source of a mass spectrometer [16]. In recoil T chemistry ion–molecule reactions, if any, are of negligible effect on the labelled product yields, whereas a very important role is played by radical reactions. Oxygen is known to act as a radical scavenger in recoil tritium reactions with hydrocarbons, *i.e.* it cleans the HT and hydrocarbons-T yields from the species produced by thermal radicals reactions. On Table II there is a comparison between the effect of added oxygen to the butane + T* and butane + T* + $Ni(CO)_4$ systems. In both cases the product yields are sharply reduced in comparison with corresponding experiments without oxygen; HT is reduced to the pure hot yield, but the total yield is higher when the metal carbonyl is present, because the hydrocarbons yield, though lower than in the experiments without $O_2$, is not reduced to the pure hot yield. It is then evident that there is a kind of competition between $O_2$ and carbonyls in the reactions with radicals, T and alkyls. Oxygen scavenges thermal radicals to suppress any further reaction with the substrate, whereas the metal carbonyl seems to react with thermal radicals as a scavenger, but it does not inhibit their further reactions; it just modifies their reactivity with the surrounding molecules causing a change in the final product yields. This means that an intermediate product from the reaction between thermal radicals and metal carbonyl (or its decomposition products) is responsible for the effects observed on the final yields. It also appears that the thermal radical concentration is the limiting factor for the formation of the reaction intermediate. This model can be tested by increasing the radical concentration by both moderation, which increases the yield of thermal T-radicals, and low pressure unimolecular decomposition of excited T-substituted molecules, which enhances the yield of alkyl radicals.

The best inert moderator for recoil T atoms is He; unfortunately, because of its high ionization potential, some $T^+$ ions react with the substrate before neutralization [17]. Ne was then used as the next best moderator, though at 92% of Ne the moderation is not as effective as desired. Nevertheless, as appears from the first two columns of Table III, the combined effect of the metal carbonyl and the radicals on the product yields is enhanced, particularly for ethylene.

Even though butane does not suffer large excitation decomposition [18], the experiments summarized on the last four columns of Table III show again that thermal radicals are responsible, together with the carbonyl, for the effect observed on the product yield.

On the basis of the above results it appears that the thermal processes which accompany the hot reactions may be modified by the presence of the metal carbonyls. It may be supposed that, in absence of a radical scavenger, thermal species will react mainly with the metal carbonyl giving reactive intermediates, of unknown structure, which will be denoted as XT• or XRT•, for T• and alkyl-T• radical respectively.

The more important reacting intermediate appears to be XT• which reacts with butane according to two main reaction paths: a) interaction with C–H bonds, and b) interaction with C–C bonds.

In case a) the reaction is a hydrogen substitution reaction (exchange reaction), leading to labelled butane as observed in all the experiments, particularly in the Ne moderated system where the yield of thermal T• is supposed to be higher than in unmoderated systems.

In case b) both 1–2 and 2–3 carbon–carbon bonds could be involved in the reaction. When the reaction takes place on 1–2 bond both $CH_3T$ and $C_3H_7T$ could be formed:

$$XT^\bullet + CH_3\text{-}C_3H_7 \rightarrow CH_3T \text{ or } C_3H_7T + \text{ unlabelled products} \qquad (1)$$

If the reaction occurs on the 2–3 bond, ethylene or ethane are the reaction products:

$$XT^\bullet + C_2H_5\text{-}C_2H_5 \rightarrow C_2H_3T \text{ or } C_2H_5T + \text{ unlabelled products} \qquad (2)$$

Reaction (2) appears to be preferred over reaction (1) and the ethylene production from reaction (2) over ethane formation, probably because of XT• structure, rearrangements and collision geometry. Enhanced yields of ethylene-T in recoil tritium reactions with ethane have been previously observed by Cipollini and Stoklin [19] and by Johnson and Urch [20]; in both cases it has been understood by Urch [21] as a consequence of the formation of a particular collision complex.

The intermediate containing the alkyl radical XRT• seems to be less reactive than its analogue with tritium. In fact it appears to react with the substrate mainly by hydrogen abstraction, leading to light hydrocarbons:

$$XRT^\bullet + C_4H_{10} \rightarrow HRT + \text{unlabelled species} \qquad (3)$$

whereas the addition of RT• radicals to the substrate is forbidden.

Though the nature and the structure of the proposed intermediates XT• and XRT• is at present unknown, it clearly appears that the added metal carbonyls cause a sharp change in the reaction path of the thermal radicals with the substrate molecules. The production of carrier free, high specific activity molecules is one of the goal of the hot atom chemistry. The method presents some limitations, which sharply decrease the potential applicability of the recoil labelling method: the parent labelled molecules are not carrier free and the secondary products, while carrier free, are in too low yields. Though the yield modifications induced by both $Ni(CO)_4$ and $Fe(CO)_5$ on butane + T* and other alkane + T* systems (1) are not large enough to be immediately used for practical purposes, the addition of species as metal carbonyls, which appear to pilot some thermal reactions along less randomized reaction paths could be of great interest for the labelling chemistry.

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## References

1 M. Castiglioni and P. Volpe, *Radiochem. Radioanal. Letters,* (1979) in press.

2 G. C. Bond, 'Catalysis by Metals', Acad. Press, N.Y., 1962, p. 2.

3 G. Stocklin, 'Chimie des Atomes Chauds', Masson, Paris, 1972, p. 69.

4 M. Castiglioni and P. Volpe, *Gazz. Chim. Ital., 102,* 709 (1972).

5 A. H. Rosenberg and R. Wolfgang, *J. Chem. Phys., 41,* 2159 (1964).

6 P. Estrup and R. Wolfgang, *J. Am. Chem. Soc., 82,* 2660 (1960); W. Ergersinger, jr., *J. Phys. Chem., 67,* 976 (1963).

7 S. C. Davis and K. J. Klabunde, *J. Am. Chem. Soc., 100,* 5973 (1978).

8 F. E. Shephard, *J. Catalysis, 14,* 148 (1969); J. H. Sinfelt and D. S. C. Yates, *J. Catalysis, 8,* 82 (1967); J. H. Sinfelt and D. S. C. Yates, *J. Catalysis, 10,* 362 (1968).

9 H. Matsumoto, Y. Saito and Y. Yoneda, *J. Catalysis, 19,* 101 (1970).

10 G. C. Bond, 'Catalysis by Metals', Acad. Press, N.Y., 1962, p. 395.

11 G. C. Bond, *ibidem,* p. 407.

12 D. Urch and R. Wolfgang, *J. Am. Chem. Soc., 83,* 2982 (1961).

13 M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc., 93,* 4924 (1971).

14 W. P. Anderson, N. Hsu, C. W. Stanger jr., and B. Munson, *J. Organometal. Chem., 69,* 249 (1974).

15 J. Allison and D. P. Ridge, *J. Organometal. Chem., 99,* C11 (1975).

16 M. Castiglioni, G. A. Vaglio and P. Volpe, unpublished results.

17 D. Seewald and R. Wolfgang, *J. Chem. Phys., 47,* 143 (1967).

18 H. N'Guyen Cong and J. M. Paulus, *Radiochem. Radioanal. Letters, 23,* 85 (1975).

19 R. Cipollini and G. Stocklin, *Radiochim. Acta, 9,* 105 (1968).

20 A. J. Johnston and D. S. Urch, *Radiochim. Acta, 20,* 120 (1973).

21 D. S. Urch, *Radiochim. Acta, 18,* 176 (1972); D. S. Urch, *Tetrahedron, 28,* 6007 (1972).